# THE VISCOSITY OF MERCURY UNDER PRESSURE.

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## CONTENTS.

## INTRODUCTION.

In a previous communication,[1] results have been given for the effect of pressure up to 12000 kg/cm$^2$ on the viscosity of 43 liquids. These liquids varied greatly in complexity, from $CS_2$ and $H_2O$ on the one hand, to Cineole ($C_{10}H_{16}O_5$) and Oleic acid ($C_{15}H_{33}COOH$) on the other. A simple generalization suggested by those experiments was that the percentage effect of pressure on viscosity is greater for those liquids which have a more complicated molecule. Hence the interest of extending the measurements to a substance with as simple a molecule as possible is obvious, and mercury, which is monatomic, at once suggests itself. In this paper the results of such measurements on mercury are recorded; these measurements were made at 30° and 75° up to 12000 kg.

The viscosity of mercury under pressure has been previously measured by Cohen and Bruins,[2] who determined the effect of 1500 kg at 20°.

## The Method.

The method previously used for 43 liquids demanded that the liquid be an electric insulator, and so was not applicable to mercury. It proved unexpectedly difficult to devise another method, and a number of attempts were made without success. The first attempt was with a modification of the method used with other liquids, in which a magnetized steel weight rose through a mass of mercury, the motion of the weight being indicated outside the pressure apparatus by the current induced in a solenoid. This device failed because of the great irregularities arising from the failure of the mercury to wet the walls of the containing vessel, so that solid friction entered. The performance was somewhat improved by amalgamating the

walls of the vessel, but the amalgamation of the steel was only temporary and partial and the improvement was not sufficient. Next, various flow schemes through glass capillaries were tried. These failed either because of my inability to seal platinum contacts into glass in such a way that the glass did not crack under high pressure because of the differential compressibility, or because the glass itself cracked when made in at all complicated shapes, or because of irregular surface tension effects due to the necessary small size of the apparatus.

Somewhat more successful was a capillary flow apparatus constructed of steel, in which about 50 gm of mercury ran of its own weight from one end of a vessel with two compartments to the other through a steel capillary coil 15 cm. in length and 0.05 cm. in diameter. A great many measurements were made with various modificatons of this general scheme. The individual results were of a high degree of irregularity, but by making a great many readings a rough value for the effect of pressure was found. The method did not work well at 75°, however, the various irregularities becoming much greater, and I was particularly anxious to get the effect of temperature, in order to find whether there is a simple connection between viscosity and volume, a matter of considerable theoretical importance.

The difficulty with all these methods arose primarily from irregular surface effects because of the failure of the mercury to wet the containing vessel. It presently became obvious that the mercury must wet the walls of the vessel if regular results were to be obtained, and I could think of no other way of doing this than making the vessel of copper, or some similar metal, and amalgamating it. I was long reluctant to do this because of my dislike to introduce impurities into the mercury, but I decided finally that this was the lesser of two evils. Professor Richards[3] had found by careful measurements that mercury dissolves less than 0.02% of copper, so that very little error is to be expected from the impurity of copper, and doubtless my early scruples were without foundation.

The general scheme of the apparatus finally adopted is shown in Figure 1. It consists essentially of two copper reservoirs partly filled with mercury, and connected by a capillary tube of copper. The apparatus could be tipped back and forth through a definite angle, and the time of flow to a definite height in either reservoir determined by the closing of an electric circuit through a platinum contact. Success was not immediate, however, even when the apparatus was constructed of amalgamated copper. Great trouble was always experienced from the contacts. In use, the surface of
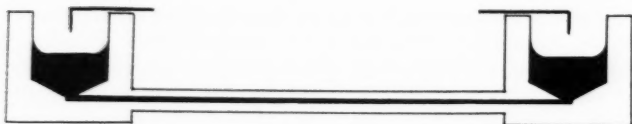
FIGURE 1.   Section of the flow part of the apparatus for determining the viscosity of mercury.   The reservoirs may be tipped in one direction or the other through a fixed angle, and the time of flow determined by means of the platinum contact.

the mercury rapidly becomes covered with a coating of dirt, so that a high potential is necessary to overcome the contact resistance.   For this purpose the current from the same magneto was used that had been used in the previous work with 43 liquids.   Such a high potential may introduce serious errors, however, because the dirt, whatever it is, has conducting properties, so that the contact may be formed by a spark jumping to the dirt on the surface of the mercury, or dirt may actually hang in whiskers to the platinum point, again closing the circuit too soon.   In the effort to minimize this effect, the top of the reservoir was narrowed down to a small neck, as shown in Figure 2, so that the contact was made with the surface of mercury
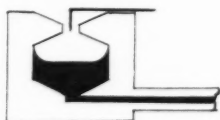


FIGURE 2.   An early form of reservoir, designed to give greater sensitivity. It was discarded because of the error from the unknown effect of pressure on the capillary action.

when it was moving comparatively rapidly, thus reducing the time error resulting from a conducting film of constant depth on the surface of the mercury, or from whiskers of definite length.   This device did not, however, produce markedly more regular results, and it was given up because of a serious theoretical objection to it, namely the head of mercury in the two reservoirs differs from that calculated from the difference of height by the amount contributed by the capillary forces in the surfaces in the two reservoirs.   This capillary effect does not vanish if the cross section of the two reservoirs is not the same.   Furthermore, it varies with pressure in an entirely un-

known way, and hence introduces an entirely unknown error into the pressure coefficient of viscosity. It seemed, therefore, that the only safe course was to eliminate the effect altogether by making the cross sections of the two reservoirs everywhere the same, so that there is no differential capillary action, and the driving pressure can be calculated simply from the difference of height.

The liquid by which pressure is transmitted is a matter of some importance, because obviously its compressibility must be known, as the effective head driving the mercury from one reservoir to the other is determined by the difference of density between mercury and the surrounding liquid. The transmitting liquid must also be of low viscosity at every pressure, so as not to effectively increase the total viscosity by the act of completing the return flow from one reservoir to the other. Ether has these properties, and it was used in a number of the experiments. Its use had to be given up, however, because the short-circuiting effects were so bad. Apparently ether decomposes under the passage of the spark at high pressures, giving some decomposition product of comparatively high conductivity, perhaps water. This seems to be a purely high pressure phenomenon; attempts to reproduce it by sparking under ether to mercury at atmospheric pressure have failed. The performance was improved by replacing ether by petroleum ether. This latter, being a hydro-carbon, can give no water on decomposition, and this theoretical expectation was justified. The compressibility of petroleum ether was not known however, and it was therefore necessary to make a special determination of it, although not with a high degree of accuracy, since it was to be used only in a correction term.

The method by which the copper is amalgamated was also found to be of great importance. At first the copper was amalgamated with sodium amalgam, washing away the sodium in the form of hydroxide with water as carefully as possible. It is probable, however, that this washing was never complete. Always after amalgamation in this way, the dirt which formed on the surface after contact had been made a number of times, was of a disagreeable mechanical texture, difficult to break through, and very apt to form whiskers on the platinum points, particularly at 75°. The trouble disappeared on amalgamating with $HgNO_3$, again washing away the salts with water as thoroughly as possible. Under these conditions dirt still formed on the surface, but its mechanical texture was entirely different, being a light powder like lamp black, without the bad effects on the contacts of the other. The apparatus with which the final measurements were made was amalgamated in this way.

The experimental procedure with the final apparatus was as follows. The apparatus was first amalgamated by filling it with an HgNO₃ solution, and then washing with many changes of water. The capillary was amalgamated and washed by pulling through it a thread with a closely fitting knot. After amalgamating and drying, a weighed amount of mercury was placed in the reservoirs, enough to fill them about two-thirds full. The reservoirs with mercury were now attached to the insulating plug, connections made to the platinum contacts, and viscosity apparatus and plug placed together, in a horizontal position, as a single assembly, in the pressure cylinder. The pressure part of the apparatus was in all respects the same as that used formerly with 43 liquids. Because of the necessity of maintaining the mercury cups always in a vertical position, the details of the insulating plug formerly used had to be modified. The former plug, which carried in a single piece the insulation and the threaded part with which the hole in the pressure chamber was closed, was now made in two parts. One part carried the insulation, and together with the copper reservoirs constituted a single assembly which could be thrust without rotation into the pressure chamber. The other part carried the thread, and was turned up against the other part, compressing the packing and closing the hole. It is not necessary to go further into the details of this construction, which was sufficiently straightforward.

The pressure chamber could be rotated back and forth through fixed angles, which were determined by suitably placed stops. The mercury was run from one reservoir to the other while the apparatus was inclined to the horizontal at approximately 11°. The timing clock was stopped by the making of contact, through a system of relays actuated by the magneto in much the same way as in the previous work. Immediately when the clock stopped, the pressure chamber was turned back to a smaller angle, about 4°, which trial had shown was the angle at which the mercury just makes contact with the platinum point. In this position a sufficient time was allowed for the mercury to come to equilibrium, assuming the same level in the two reservoirs. The run was now started by rotating the pressure chamber from an inclination of 4° on one side to an inclination of 11° on the other side. The clock was so connected with various contacts that it started to run simultaneously with the rotation, the rotation itself occupying only a negligible time. In the early work the clock was started on breaking the contact with the platinum point, but the breaking contact proved much less reliable than the making contact,

because of danger of dirt sticking to the point, and in all the later
work the clock was started with the rotation.

At each pressure, ten readings of the time of flow were made,
five in each direction, and the mean taken. No attempt was made to
set up the apparatus perfectly symmetrically, so that the time of
flow on the two sides was never exactly the same. In fact, it would
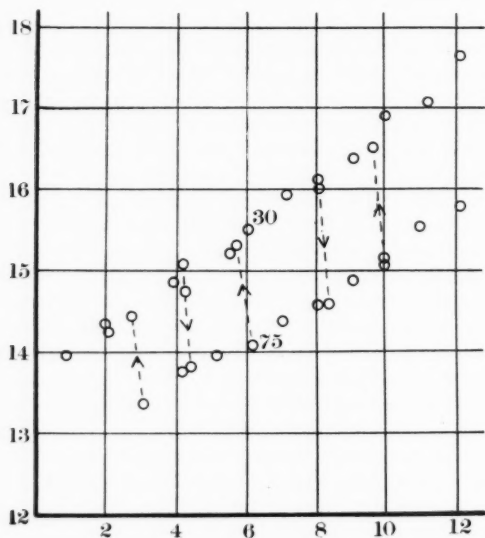not have been possible to attain symmetry at all pressures, even if



FIGURE 3. The observed times of flow in seconds plotted against pressure
in thousands of kg/cm² at 30° and 75° C. The circles connected by dotted
lines refer to readings obtained by changing the temperature at approximately
constant pressure. The other readings were obtained during constant
temperature runs by varying the pressure.

it had been attained at one, because unequal yielding of the packing
at different pressures throws the apparatus out of allignment. The
five readings for one direction of flow varied in consistency; when the
apparatus was working well, the extreme variations were not more
than 1 or 2 per cent, and from this they might rise to 3 or 4.

Readings were made at a number of pressures over the range from

0 to 12000 at 75°, and then at 30°, and then the temperature was changed from 30° to 75° and back a number of times at each of several different pressures, this giving direct measurements of the temperature coefficient of viscosity at a number of different pressures. This latter procedure was adopted to more certainly fix the temperature coefficient, and ensure that there had been no permanent changes produced in the apparatus during the readings at constant temperature.

The experimentally observed times are shown in Figure 3.

## Corrections.

A number of corrections must be applied to the directly measured times in order to obtain the changes of viscosity. Unlike many of the other pressure effects which I have measured, these corrections are large, amounting altogether to the total magnitude of the measured effect, so that it will be necessary to give a careful discussion of them.

A determination of the corrections involves an accurate solution of the flow problem. The conditions of our problem differ in two important respects from the simple flow problem usually treated in connection with experimental determinations of viscosity, in that firstly, flow takes place under a pressure difference which varies so much from the beginning to the end of flow that the results cannot be simply expressed in terms of the average pressure difference, and secondly, the so-called kinetic energy correction is large, and varies in amount at different pressures. Allowance for variable head may be simply made by writing the equation of flow in differential form and integrating it, but the kinetic energy correction requires more discussion. The flow here is from one reservoir to another, the reservoirs themselves being so large that the kinetic energy of the rise and fall of the liquid in the reservoirs may be entirely neglected, so that we have to consider only the kinetic energy of the liquid in the capillary as it flows from one reservoir to the other. Now it is the opinion of Grüneisen[4] that the kinetic energy correction should not be applied under these conditions, the argument being that there is no net increase of kinetic energy of the liquid. Grüneisen considers that the correction for turbulence is much more important. Cohen,[5] in discussing his own experiments, has quoted Grüneisen with approval. It is, however, not the classical opinion that the kinetic energy effect may be neglected under such conditions, as may be found set forth at length in Bingham's book.[6] It is my belief that the classical point of view is correct in this case, as I shall try

to show by the following argument. This argument is restricted by the assumption that there is no turbulence in the capillary itself, and that the rate of rise of the liquid in the reservoirs is not fast enough to disturb the equilibrium configuration of the surface. We also neglect end effects in the tube near its mouth. The length of the tube of these experiments was 160 times the diameter, so that doubtless this condition was satisfied.

We now consider the flow of the liquid in three parts; that in the higher reservoir, where the liquid gains kinetic energy, that in the capillary, where conditions of steady flow prevail, and that in the lower reservoir, where the kinetic energy of the flow in the capillary is dissipated. The energy condition evidently controls the situation. There is a decrease of potential gravitational energy during flow (or of pressure energy if the flow takes place between two reservoirs under a pressure difference) which is evidently all dissipated as heat. This dissipation takes place primarily in two places: in the capillary, where the viscous forces of the liquid are overcome, and in the lower reservoir, where the kinetic energy of the liquid emerging from the capillary is degenerated into heat energy. There is also some generation of heat in the higher reservoir, where the liquid acquires kinetic energy just before it enters the capillary, because in this region where velocity is gained, different parts of the liquid move with different relative velocities, and this necessarily involves viscous dissipation, but it seems safe to assume that by far the larger part of the gain of velocity in this region is produced by the reversible action of simple mechanical pressures, and that the irreversible aspects are relatively unimportant.

The amount of viscous generation of heat in the capillary may be calculated by the classical analysis by simply setting the heat equal to the difference of $pv$ energy as the liquid flows through the tube, neglecting of course the compressibility, and the thermal expansion of the liquid under the heating. The rate of flow is determined by the pressure difference, so that the heat generation may be expressed in terms of the rate of flow. Of course in working out the exact expressions, integrations across the section of the tube are necessary because the velocity varies throughout the tube. In the lower reservoir the heat generated is equal to the kinetic energy of the entering liquid, and this again may be expressed in terms of the rate of flow. Finally, the sum of these two amounts of energy is equal to the loss of energy of position, and this again can be expressed in terms of the rate of flow. The resulting equation is a cubic

in terms of the rate of flow ($= dV/dt$), from which $dV/dt$ may be once cancelled, giving:

$$\frac{\rho}{\pi^2 R^4}\left(\frac{dV}{dt}\right)^2 + \frac{8l\mu}{\pi R^4}\frac{dV}{dt} - g\rho(h_2 - h_1) = 0, \tag{I}$$

in which $\rho$ is the density of the liquid (or the difference of two densities if the apparatus is immersed in another liquid as in the pressure experiments), $R$ is the radius of the capillary, $l$ its length, $\mu$ the viscosity in Abs C.G.S. units, $dV/dt$ the rate of flow in cm³/sec. and $h_2 - h_1$, the difference of height of the surfaces of the liquid in the two reservoirs.   In this equation, the first term comes from the loss of kinetic energy, the second from the viscous dissipation in the capillary, and the third is the loss of gravitational potential energy.

This equation may now be compared with that given by the classical analysis, and will in fact be found to be exactly Bingham's equation (8) on page 18, except that the first term in Bingham's equation differs from ours through a numerical factor "$m$".   In fact, the simple analysis given by Bingham makes $m = 1$, but a more elaborate analysis due to Boussinesq makes $m = 1.12$.   The argument above shows that in fact $m$ should be larger than 1 because of irreversible effects in the higher reservoir, where the liquid is gaining energy.

It seems to me, therefore, to be not open to question that the kinetic energy correction should be applied, under the conditions of these experiments, and in working out further the corrections I have assumed the flow equation (I), except that the first term is multiplied by Boussinesq's factor 1.12.

Entirely apart from this theoretical argument, we have the experimental fact that when the kinetic energy correction is applied, the experimentally determined temperature coefficient of viscosity at atmospheric pressure agrees with that of other observers, whereas without the correction, the experimental value is 40% too low.

Equation (I), with $m = 1.12$, may now be solved for $dV/dt$, and integrated for $T$.   I find:

$$T = \frac{m\rho}{4\pi\mu l}\int_0^{V'} \frac{dV}{\sqrt{\alpha + \beta V - 1}}, \tag{II}$$

where

$$\alpha = 1 + \frac{m\rho R^4}{16\mu^2 l^2}\,g\rho(h_2 - h_1)_0,$$

and

$$\beta = \frac{m\rho R^4}{16\mu^2 l^2}\, g\rho\, \frac{(h_2 - h_1)' - (h_2 - h_1)_0}{V'}.$$

The integration may be explicitly carried out, and a closed formula found, which involves the logarithms of expressions containing radicals. In practice, of course, $T$ is the measured quantity; $\mu$ is the unknown, and the above relation is to be solved for $\mu$ in terms of $T$ and other experimentally determinable quantities which enter the relation. Now an examination of the relation shows that $\mu$ enters in a most complicated way, and the only method of solution is by successive approximations in any special numerical case. It is natural therefore to seek for some method by which an approximate solution of the relation for $\mu$ may be found. An examination of the equation shows that the complication is introduced by the fact that the relative importance of the kinetic energy term compared with the principal viscous term varies as the head varies. But the effect of this is in the nature of a correction on a correction, and may therefore presumably be approximately treated. Let us in equation (I) substitute for $dV/dt$ the average rate of flow, which may be written as $V'/T$. Equation (I), with $m = 1.12$, may now be solved for $\mu$, giving:

$$\mu = \frac{\pi g R^4}{8V'l}\, g\rho(h_2 - h_1)_{av}T - \frac{1.12\rho V'}{8\pi l} \cdot \frac{1}{T} \qquad \text{(III)}$$

$$= AT - \frac{B}{T}. \qquad \text{(IV)}$$

In this equation, which is only approximate, everything on the right hand side may be determined except $(h_2 - h_1)_{av}$, which is evidently not a space average, whereas the space average is the only sort of average that can be determined experimentally under our conditions. Equation (IV) may be solved for $A$ if $\mu$, $B$, and $T$ are known.

We now have to consider the question whether equation IV is a sufficiently good approximation over the range of these experiments. The answer can be found by comparing with the results of the exact equation. The test was made in the following way. Into the exact equation, I, was substituted the constants of the apparatus and the viscosity of mercury at atmospheric pressure, giving a value of $T$. With these values, the constant $A$ of the approximate equation, IV, was calculated. Keeping now the same values of the constants of the apparatus, a 33% higher value for $\mu$, which experiment and rough

corrections had shown to be the approximate value at 12000 kg, was substituted into the exact equation, and the value of $T$ again found. This value for $T$ was next put back into the approximate equation, IV, in which we now know both constants $A$ and $B$, and the value of $\mu$ computed. This value should be the same as that put into the exact equation, and as a matter of fact, it did agree with it within $\frac{1}{4}\%$, showing that the approximate equation IV is a sufficiently good approximation for $\mu$ over the range of these experiments.

Granting now the allowability of the approximate formula IV, the determination of the various corrections becomes much simplified, although it is still complicated enough. The coefficient $A$ is what would be given by the classical analysis without the kinetic energy correction, taking account, however, of the variation of head during flow, which means integrating a differential equation. The classical equation for this is:

$$\frac{dV}{dt} = \frac{\pi g}{8} \frac{R^4}{\mu l} \Delta p.$$

Here of course $\Delta p$ is a function of the volume that has flowed, and during flow at constant pressure and temperature is a linear function. Hence the equation reduces to the form:

$$\frac{dV}{a - bV} = \frac{\pi g}{8} \frac{R^4}{\mu l} dt.$$

This may be integrated and solved for $\mu$. Since the $\mu$ obtained from this equation is uncorrected for the kinetic energy effect, we may denote it by $\mu_{unc}$, and write $\mu_{unc} = AT$, where $A$ has the value:

$$A = \frac{\dfrac{\pi g R^4}{8l} b}{\log \dfrac{a}{a - b(h_1' - h_{10})S}}$$

where

$$a = \rho \left[ l \sin \theta_2 - \cos \theta_2 \left( 2h_{10} - \frac{1}{S} V_{Hg} \right) \right]$$

and

$$b = \frac{\rho}{S} 2 \cos \theta_2.$$

In this formula the letters which have not been already explained are: $S$ = cross section of the reservoirs, $V_{Hg}$ = total volume of the

mercury in the apparatus, $h_{10}$ the height of the mercury in the reservoir toward which flow takes place at the instant of beginning of flow, and $h_1'$, the final height at the instant of making contact in the same reservoir, and $\theta_2$ is the angle of inclination with the horizontal of the apparatus during flow. $h_{10}$ is determined by the constants of the apparatus and the angle, $\theta_1$, from which flow was started.

The quantity $A$ above, since it contains the dimensions of the apparatus and the density of the liquids, is obviously a function of pressure. If, as a matter of notation, we write

$$A = \frac{\pi g R^4}{8l} \frac{b}{\log I},$$

then we shall obviously have

$$\left(\frac{\mu_p}{\mu_0}\right)_{\text{unc}} = \frac{T_p}{T_0} \cdot \frac{A_p}{A_0},$$

where the subscripts $0$ and $p$ denote respectively the values at atmospheric pressure and pressure $p$. The change with pressure of the factor $(\pi g R^4/8l)b$ can at once be written down by inspection, so that we have:

$$\frac{A_p}{A_0} = \frac{(\rho_{\text{Hg}} - \rho_l)_p}{(\rho_{\text{Hg}} - \rho_l)_0} (1 - \kappa_{\text{Cu}} p) \frac{\log I_0}{\log I_p}.$$

Here we have put explicitly $\rho = \rho_{\text{Hg}} - \rho_l$, where $\rho_{\text{Hg}}$ is the density of mercury and $\rho_l$ the density of the transmitting liquid. $\kappa_{\text{Cu}}$ is the linear compressibility of copper.

The term $\log I_0/\log I_p$ is more complicated to work out as a function of pressure, but it is a straight forward job, in terms of the dimensions of the apparatus, and the known distortions under pressure, remembering the initial conditions, namely that the liquid is adjusted before flow starts by inclining the apparatus at a fixed angle independent of pressure, that flow takes place also at a fixed angle independent of pressure, and that flow terminates when the mercury strikes a fixed contact whose position is subject to the pressure distortion of the apparatus.

The dimensions of the apparatus were such that under 12000 kg. log $I$ increases by nearly 5.5%. The density of mercury, which enters the formula, can be taken from previous experiment,[7] as can also the compressibility of copper.[8] The transmitting liquid, however, for which petroleum ether was chosen for reasons already described, had not had its compressibility previously determined, and a special

determination was necessary. A rough determination was good
enough for the present purpose. This was made in a new apparatus,
which has been previously used and described in connection with a
measurement of the compressibility of glycerine.[9] The following
values for the density were found (Table I).

### TABLE I.

DENSITY OF PETROLEUM ETHER AT 30° C.

| Pressure Kg/cm² | Density |
|---|---|
| 1 | .638 |
| 2000 | .742 |
| 4000 | .792 |
| 6000 | .825 |
| 8000 | .849 |
| 10000 | .872 |
| 12000 | .889 |

The values of $A$ so far discussed are for 30° C. The value at
75° may be found by a discussion exactly like that given above for
the effect of pressure, since obviously the distortion produced by
a change of temperature is exactly like that produced by a hydrostatic
pressure. The results of the calculation are contained in Table II,

### TABLE II.

RELATIVE VALUES OF "$A$" (SEE TEXT) AS A FUNCTION OF PRESSURE AND
TEMPERATURE

| Pressure Kg/cm² | A | |
|---|---|---|
| | 30° | 75° |
| 1 | 1.000 | 1.002 |
| 2000 | .989 | .991 |
| 4000 | .983 | .985 |
| 6000 | .977 | .979 |
| 8000 | .971 | .974 |
| 10000 | .969 | .971 |
| 12000 | .966 | .968 |

which shows the correction to be applied to the value of $A$ at 30°
and atmospheric pressure in order to obtain the value of $A$ at higher
pressures and at 75°.

If instead of integrating the equations of flow, one had used the less exact equation obtained by supposing flow to take place at a constant head equal to the mean of the initial and the final heads (that is a space average instead of a time average) the correction factor for $A$ at 30° and 12000 kg. would have been found to be 1–0.046 instead of 1–0.034, as given by the more accurate calculation above.

We next have to determine the variation with pressure of the coefficient in the kinetic energy correction, that is, the correction of $B$ ($ = 1.12\rho V/8\pi l$).     Since this term is comparatively small, it will be sufficient to assume that the variation of $B$ with pressure is linear. The same data used in calculating the value af $A$ at 12000 give for $B$ at 12000 a 6.6% correction.   The correction at 75° may be similarly found.   Table III gives the results.

TABLE III.

RELATIVE VALUES OF "$B$" (SEE TEXT) AS A FUNCTION OF PRESSURE AND TEMPERATURE.

| Pressure Kg/cm² | B | |
|:---:|:---:|:---:|
| | 30° | 75° |
| 1 | 1.000 | .988 |
| 2000 | 1.011 | .999 |
| 4000 | 1.022 | 1.010 |
| 6000 | 1.033 | 1.021 |
| 8000 | 1.044 | 1.032 |
| 10000 | 1.055 | 1.043 |
| 12000 | 1.066 | 1.054 |

We are now ready to correct the observed values of time, except for the absolute values of $A$ and $B$.   An examination of the formulas for $A$ and $B$ shows that $A$ is subject to considerable experimental error, through the factor $R^4$, whereas $B$ involves only $\rho$, $V$, and $l$, which may be all easily measured.   It appeared therefore that the most accurate method of getting $A$ was to calculate $B$, and then substitute in equation IV the experimentally measured $T$ and the absolute value of $\mu$ determined by other experimenters, and solve for $A$.   The value adopted for $\mu$ at 30° and atmospheric pressure was 0.01514, as the best of all the values given in Landolt and Börnstein.   The values so found for $A$ and $B$ were 0.001372, and 0.0497, respectively.

We are now in a position to calculate the viscosity at various pressures and at 30° and 75° in terms of the measured times of flow. In doing this, smooth curves were drawn through the experimentally determined times, and the times read from these curves at intervals of 2000 kg. These times were now corrected as above, and the results obtained which are shown in Table IV.

TABLE IV.

VISCOSITY OF MERCURY AS A FUNCTION OF PRESSURE AND TEMPERATURE.

| Pressure Kg/cm² | Absolute Viscosity 30° | 75 | Percentage Increase of Viscosity 30° | 75° |
|---|---|---|---|---|
| 1 | .01516 | .01341 | 0.0 | 0.0 |
| 2000 | .01588 | .01399 | 5.1 | 4.6 |
| 4000 | .01663 | .01463 | 9.9 | 9.6 |
| 6000 | .01742 | .01528 | 15.2 | 14.4 |
| 8000 | .01825 | .01599 | 20.0 | 18.8 |
| 10000 | .01913 | .01675 | 26.3 | 24.7 |
| 12000 | .02008 | .01757 | 33.5 | 31.1 |

*Checks on the Measurements.*

The absolute value of viscosity cannot be calculated with much accuracy from these measurements because of the difficulty, already mentioned, of measuring the absolute dimensions of the capillary. There is, however, a check that may be applied, by comparing the temperature coefficient between 30° and 75° with that determined by other observers. In Figure 4 are plotted all the values of viscosity between 0° and 100° listed in Landolt and Börnstein's tables. In the same diagram are shown, as double circles, the values given above in Table IV; of these the value at 30° was assumed in determining one of the constants, and the 75° value was then calculated in terms of the experimental data. This value is seen to fall within the range of previous experimenters, and in so far gives presumptive evidence of the correct functioning of the apparatus.

It is perhaps worth while to mention the results obtained with the various forms of preliminary apparatus. It must be remembered that all these results were very irregular, that the apparatus would hardly function at all at 75°, and that we can expect from them only a correct order of magnitude for the effect. The first of the preliminary forms of apparatus which gave at all consistent results was
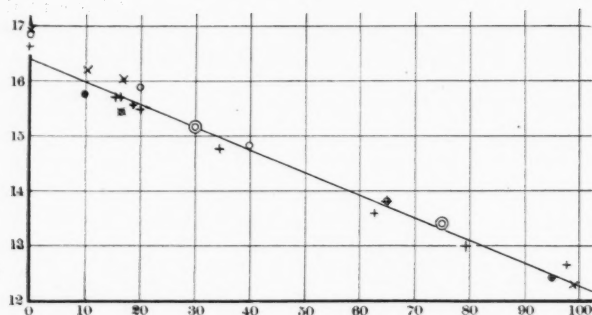
FIGURE 4. Collection of the data given in Landolt and Börnstein's Tables for the viscosity of mercury as a function of temperature at atmospheric pressure. Abscissae are Centigrade degrees, and ordinates 1000 times the absolute viscosity. The different symbols refer to data of different observers. The double circles refer to the data of this paper. The constants were so chosen that the point at 30° should fall on the curve of other observers. The closeness with which the double circle at 75° falls on the line measures the agreement of my temperature coefficient with that of other observers.

that of flow through a coiled steel capillary. The pressure cylinder was inverted through 180° in this experiment, with the result that the capillary was completely emptied at every reversal, and the walls wet with the transmitting liquid. During the flow, therefore, the mercury had to push away from the walls of the capillary a film of transmitting liquid. Since the viscosity of the transmitting liquid increases under pressure much more rapidly than that of mercury, this apparatus would be expected to give too high an increase of viscosity with pressure. The actual value found from a number of measurements with this apparatus, after applying a rough correction for the kinetic energy effect, was an increase of 40% at 30° and 12000 kg, against 33.5% found with the final apparatus above. This 40% was the mean of three separate runs, differing from the mean by 6% of the coefficient (that is varying from 42.4% to 37.6%). Beside the steel capillary coil apparatus, several forms of tipping apparatus, more or less like the final one, were used before success was attained. These preliminary attempts failed because of dirt on the surface of the mercury sticking to the platinum contacts, making the time of flow too short. Since the effect became larger at higher pressures, the pressure coefficients found with this apparatus were too low.

The first of these preliminary tipping apparatuses had a capillary smaller than the final one, so that the time of flow was three times greater. Under these conditions the kinetic energy correction may be neglected. This apparatus gave for the increase at 30° at 12000 the value 24.5% when the transmitting liquid was ether, and 25% with petroleum ether. A second form of apparatus, which was muck like the final one, so that the same corrections could be applied to it, gave an increase of 26%.

We now have to compare the results above in Table IV with the only previous determination of the effect of pressure, namely that of Cohen.[2] His measurements were made at 20° and at a single pressure, 1500 atmospheres. He found an increase of viscosity of 4.8% under these conditions. Correcting this from 20° to 30° by my results above, and changing from atmospheres to kg/cm², Cohen's result is equivalent to an increase of 6.1% for 2000 kg/cm² at 30°, against my value 5.1% above. We now seek to understand this difference. One small source of error in Cohen's work is that he has treated the flow as if it took place under a constant, instead of under a variable, head. Cohen gives a scale drawing of his apparatus, from which the dimensions may be obtained, and it appears that during flow the head varied from 6.3 to 2.1 cm. of mercury. The more rigorous equations of flow seem called for under these conditions. I find, on using the more rigorous equations that the value 6.1% given above for the effect of 2000 kg. should be reduced to 5.9%. This is not a large change, but is in the direction toward my value. There are also other possibilities of error in Cohen's work, the numerical magnitude of which are more difficult to estimate, but which work in the same direction. Thus the viscosity of the transmitting liquid, in Cohen's case, water, affects the measured results, because as mercury flows down from the high reservoir to the lower, water must flow back to take its place. Cohen's diagram does not show any channels specially made for the return flow of the water, so that the presumption is that they were small. Any such channels would become smaller at high pressure because of the compressibility of the apparatus, and furthermore water increases in viscosity at 20° under 1500 atmospheres, so that the net effect would be to give too large an apparent increase of viscosity of mercury. In my apparatus the return channel was at least 100 times greater in area than that of the capillary, and the distortion of the apparatus was in such a direction as to increase this with increasing pressure. Since the time of flow varies as the square of the section, no error from this effect is to be

expected in the values of Table IV.    Another possibility of error in
Cohen's experiment is the surface tension effect.    The electric contact
in his apparatus occurred in a constriction of about 3 mm. diameter,
the diameter of the main reservoir being 1.8 cm.    While the mercury
is in the constriction, and while it is approaching it, the difference of
surface tension at the two surfaces of unequal area is in such a direc-
tion as to oppose the flow, thus simulating too high a viscosity.    If
the surface tension increases under pressure, as seems probable,
this effect will become relatively larger at high pressures, resulting
in too high a pressure coefficient.    The kinetic energy correction,[5]
which I believe theoretically should have been applied to Cohen's
experiment, assumes a more or less academic position, because his
time of flow was so long as to make this correction numerically
negligible.    It is unfortunate that Cohen's seven repetitions of his
experiment were made under exactly the same conditions; if the
quantity of mercury had been varied somewhat we would have some
basis for an estimate of the magnitude of another possible correction,
due to the almost complete emptying of the upper reservoir, for
which there is at present no data.    All of these suggested possi-
bilities will probably, however, not have a large effect, so that it
seems likely that Cohen's value for the pressure coefficient would
remain at least 10% higher than mine.

## Discussion of Results.

If the viscosity of mercury is plotted against pressure at 30° and
75°, (Figure 5) the results will be found to be of the same general
character as those previously found for other liquids.    Viscosity
increases with increasing pressure at an accelerated rate, and the
percentage increase at 75° is less than at 30°.    It will be found on
inspection of the diagram that the curve for 75° may be obtained by
displacing bodily the 30° curve along the pressure axis by about
5750 kg.    This means that the fractional change of viscosity pro-
duced by a given increment of pressure is a function only of the vis-
cosity, no matter whether a given value of the viscosity is found
at a low pressure and low temperature or at a high temperature and a
high pressure.    The experimental data are not sufficient to allow a
similar statement about temperature coefficients at equal viscosities.
The result for the pressure coefficient was not found to hold in the
case of other liquids, so that possibly in the case of mercury the result
is only approximate, holding only over a comparatively narrow range.

The upward curvature of viscosity against pressure is slight, but
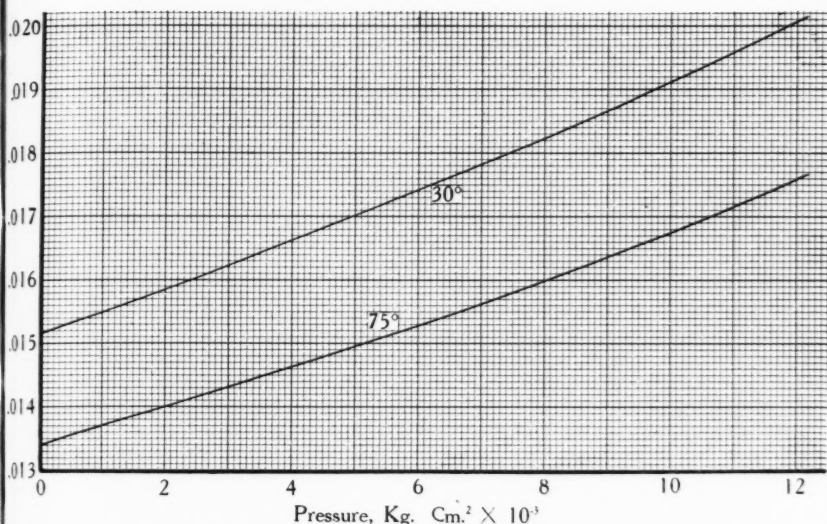is certainly beyond experimental error.

FIGURE 5.   The absolute viscosity of mercury at 30° and 75° as a function of pressure.

As compared with the results for other liquids, the viscosity of mercury is striking regarded as a volume function. With other liquids, viscosity at constant volume decreased with rising temperature, but the decrease was not large. With mercury, on the other hand, the departure from this simple relation is very marked. The volume at 75° and 2000 kg. is the same as that at 30° and atmospheric pressure, but the viscosity at 75° and 2000 kg. is 0.0140, against 0.0152 at 30° at atmospheric pressure. The pressure coefficient of viscosity would have to be nearly three times as great as found above to make viscosity a function of volume only. Such a change is of course entirely outside the possibilities of experimental error; even if Cohen's value for the pressure coefficient is adopted, essentially the same conclusion is reached. Considerable theoretical significance has been attached to the idea that viscosity is a function of volume only; the fact that the largest departure from this relation has been found in mercury, a monatomic liquid and the simplest yet investigated, would seem to be of considerable significance.

The results bear out the expectation mentioned at the beginning

of this paper that because of its simple monatomic structure the pressure coefficient would be found to be especially small in mercury. The smallest value previously found was for water, which increases 2.7 fold at 30° under 12000 kg., against an increase of only 33% for mercury. These results in general, therefore, bear out the view that in a liquid viscosity is intimately connected with some sort of interlocking mechanism between the molecules, instead of being primarily a kinetic matter, as in most theories hitherto. In our present state of knowledge it is exceedingly difficult to advance further with the picture of an interlocking mechanism and make it yield quantitative results, for the reason that we need detailed knowledge of the shape of the molecule and its deformation under pressure, which we do not have.

It is a pleasure to acknowledge the help received in most of the manipulations of this paper from my mechanician, Mr. E. T. Richardson.

THE JEFFERSON PHYSICAL LABORATORY,
Harvard University, Cambridge, Mass.

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